(E. Merck No. 9385) and a pressure-driven rate of 2.0 in./min leads to a successful separation.[28] In every instance, (*E*)-**4**-X eluted first, followed by (*Z*)-**4**-X, (*E*)-**5**-X, and finally (*Z*)-**5**-X. (*E*)- and (*Z*)-**4**-OH were chromatographed with aluminum oxide (80–200 mesh neutral) and 40% ethyl acetate in hexanes; (*Z*)-**4**-OH has a larger R_f value than (*E*)-**4**-OH.

The peak patterns in the ^{1}H and ^{13}C NMR spectra for all the oxetanes are very similar. For **6** and **7**, complete assignments of the ^{13}C peaks and full descriptions of the ^{1}H NMR spectra are given in the supplementary material.

Irradiation of 1-X and (*Z*)-3. A relatively high concentration of (*Z*)-**3** (0.3 M) was employed to favor the formation of *cis*-oxetanes **6**. A solution of 0.2 g of **1**-X and 1 g of (*Z*)-**3** in 50 mL of spectrograde acetonitrile was placed in a Pyrex tube stoppered with a rubber septum. The solution was irradiated (Xe/Hg 1-kW lamp) for 48 h (60–90% conversion) through a 313-nm filter solution (0.002 M K_2CrO_4 in 1% aqueous K_2CO_3). The solvent was removed from the light yellow solution on a rotary evaporator, and the residue was chromatographed over silica gel with ethyl acetate (4% in hexanes) as eluant. In every case, (*Z*)-**6**-X eluted first, followed by (*E*)-**6**-X, (*Z*)-**7**-X, and finally (*E*)-**7**-X. Fluorooxetanes were analyzed by means of GC with a carbowax column and separated by repeated column chromatography (silica gel). Since the diethoxyoxetanes are acid sensitive and decompose within hours after drying, they were stored in a sealed tube in a freezer.

The peak patterns in the ^{1}H and ^{13}C NMR spectra for these oxetanes are also similar (see supplementary material).

The unstable products (*E*)- and (*Z*)-**6**-Br were converted into (*E*)- and (*Z*)-**8**-Br by acid-catalyzed alcoholysis. (*E*)-**8**: ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 104.15, 79.62, 75.20, 68.70, 65.44, 65.27, 64.49, 50.06, 46.09, 45.34, 38.36, 37.87, 31.60, 31.12, 30.84, 15.73, 15.47, 15.25; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.55 (d, J = 5.4 Hz, 1 H), 3.97 (dq, J = 7.1, 9.1 Hz, 1 H), 3.81 (dq, J = 7.1, 9.1 Hz, 1 H), 3.61–3.73 (m, 3 H), 3.54 (dq, J = 7.1, 10.0 Hz, 1 H), 3.45 (dq, J = 7.1, 9.2 Hz, 1 H), 2.93 (s, 1 H, –OH), 2.61–2.64 (m, 1 H), 2.48–2.53 (m, 1 H), 1.95–2.32 (m, 9 H), 1.43–1.51 (m, 2 H), 1.16–1.24 (3t, 9 H). (*Z*)-**8**: ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 104.07, 79.78, 74.83, 68.61, 65.87, 65.50, 64.35, 49.85, 44.36, 44.18, 39.06, 38.24, 32.74, 31.99, 31.32, 15.71, 15.46, 15.20; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.54 (d, J = 5.5 Hz, 1 H), 3.41–3.97 (m, 8 H), 2.87–2.94 (m, 3 H), 1.31–2.45 (m, 10 H), 1.15–1.25 (3t, 9 H).

Acknowledgment. We thank Dr. Michael Y. Chiang for the X-ray crystal structure determination of (*E*)-**4**-F. This work was supported at Columbia by the NSF and AFOSR and at Stony Brook by the NSF. W.-S.C. thanks the Lederle Laboratory of American Cyanamid Co. for the predoctoral fellowship 1989–90.

Supplementary Material Available: ^{1}H and ^{13}C NMR data for **6**- and **7**-H, (*E*)- and (*Z*)-**6**-F and -Cl, (*E*)- and (*Z*)-**7**-Cl and -Br; mass spectral data for **4**- and **5**-H, (*E*)- and (*Z*)-**4**- and -**5**-F, -Cl, -Br, and -OH, and (*E*)- and (*Z*)-**6**- and -**7**-F and -Cl (7 pages). Ordering information is given on any current masthead page.

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Photochemistry of Stilbene–Amine. Spin-Trapping Study

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2-Methyl-2-nitrosopropane (MNP) was used as a spin-trap reagent to study the radicals formed in the photochemical reaction of substituted *trans*-stilbenes (TS) with tertiary amines. Seven 1,2-(*p*,*p*′-disubstituted phenyl)ethyl radicals were trapped by MNP and isolated and identified by HPLC-EPR. The nitrogen hyperfine splitting constants (hfsc) of these radicals are linearly correlated with the Hammett substituent constants σ_P. There is also a linear correlation of the nitrogen hfsc with both the single σ_P parameter and the dual $\sigma_{R'}$, σ_I parameters. The inductive and resonance effects are of equal importance. The correlation between proton hfsc and a single σ_P parameter is not linear. There is fair correlation between the β-proton hfsc and the dual parameters $\sigma_{R'}$, σ_I. The only fair correlation may be due to the large dihedral angle between the nitrogen π orbital and the N–C–H plane.

Introduction

The spin-trapping technique[1-3] has been useful for the study of radical species formed in various chemical reactions.[4-9] Thus, unstable free radicals can be trapped by such reagents as 2-methyl-2-nitrosopropane (MNP) and α-phenyl-*N*-*tert*-butylnitrone (PBN) to form stable nitroxide radicals that can be studied by electron paramagnetic resonance (EPR). We have used the spin-trapping technique to study the unstable free radical species formed from the *trans*-stilbene (TS)–amine exciplex system, since it has been reported that the mechanism for the photochemical reaction between TS and tertiary amines involves consecutive electron and proton transfer.[10-13] The experimental evidence for the reactive intermediates formed

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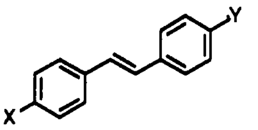
in this reaction include TS singlet, the exciplex, the TS anion radical, and the amine cation radical (aminium ion radical). It is also known that proton transfer leads to the formation of 1,2-diphenylethyl and α-aminoalkyl radical pairs.

Radical chromatography,[14] the spin-trap technique, and resolution enhancement[15,16] have been used to study this TS–amine photochemical system. Preliminary studies[17] have shown that the species trapped by MNP is the 1,2-diphenylethyl radical (R):

$$\underset{(R)}{C_6H_5CH_2\dot{C}HC_6H_5} + MNP \rightarrow t\text{-BuN(O}^{\bullet}\text{)R} \qquad (1)$$

Substituent effects on the EPR hyperfine splitting constants (hfsc) of radicals containing substituted phenyl moieties have been investigated.[18-27] We have been able to study substituent effects on hfsc of the trapped nitroxide of eq 1, where the nitroxide radical center and the substituted phenyl moiety are separated by a saturated carbon. The spin-trapping HPLC-EPR technique has been applied to study reactions of the substituted TS 1-11 with the tertiary amines triethylamine (TEA), diisopropylethylamine (DIPEA), and diisopropylmethylamine (DIPMA).



	X	Y		X	Y		X	Y
1	CH_3O	H	5	CH_3O	CH_3O	9	Cl	Cl
2	Cl	H	6	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	10	Br	Br
3	Br	H	7	CH_3	CH_3	11	CN	CN
4	CN	H	8	H	H			

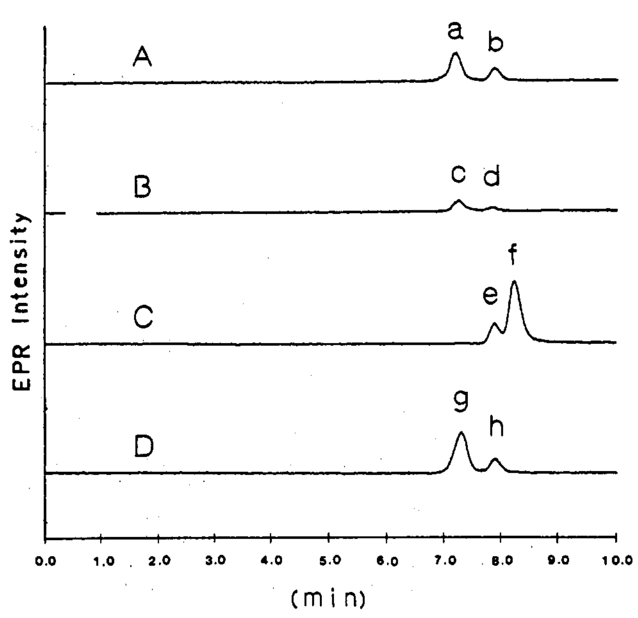


Figure 1. Chromatograms of products from photolysis of TS, DIPMA, and MNP: A = 2, B = 3, C = 5, D = 8.

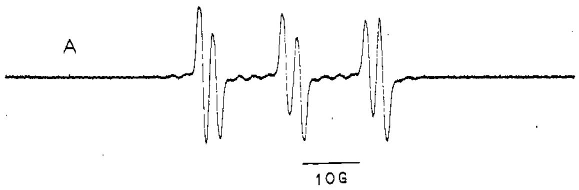


Figure 2. EPR spectrum of product from photolysis of 1, DIPMA, and MNP.

Experimental Section

The para-substituted *trans*-stilbenes were prepared from the corresponding para-substituted benzaldehyde and benzyl chloride by the Wittig reaction.[28] The para,para′-disubstituted *trans*-stilbenes were prepared from the corresponding benzaldehyde and a para-substituted benzyl chloride and were purified by recrystallization from benzene. The melting points were as follows.

compd	mp (°C)	compd	mp (°C)
5	132–134 (lit.[29] 135–136)	9	208–210 (lit.[30] 206–210)
6	129–131 (lit.[29] 130–131)	10	173–175 (lit.[31] 178)
7	180–182 (lit.[29] 179–180)	11	282–283 (lit.[30] 282–284)

Triethylamine, diisopropylethylamine, and diisopropylmethylamine were reagent grade (Merck). Ethyl acetate and *n*-hexane used for HPLC-EPR were spectroscopic grade (Merck). The spin trap reagent 2-methyl-2-nitrosopropane was prepared by a known procedure.[32]

Irradiation was carried out with a Hanovia medium-pressure mercury lamp (450 W). The EPR spectrometer (Bruker EPR 300 X-Band) was equipped with an ER 035M NMR gaussmeter, and the *g* value was measured with DPPH as internal standard. The EPR spectrometer was operated at 100-kHz modulation frequency and 9.63-GHz microwave and was connected to a Perkin-Elmer HPLC with a silica gel chromatographic column. A quartz flow cell ca. 0.5-mm i.d. and 3.0-cm long was set in the EPR sample cavity and was connected to the exit of the column with ca. 0.3-mm i.d. Teflon tubing. A 1:1 mixture of ethyl acetate and *n*-hexane was used as eluent. The chromatography conditions were as follows: pressure ca. 100 kg/cm^2, flow rate 0.5 mL/min, temperature ca. 25 °C. The microwave power was 15 db (6.3 mW). For chromatography, the magnetic field was fixed at the position indicated by the vertical arrow in Figure 3, and the magnetic field modulation was applied at an amplitude of 6.3 G to cover a wide range during the separation.

Results

1. *trans*-Stilbene with DIPMA. An acetonitrile solution of *trans*-stilbene, DIPMA, and MNP was photo-

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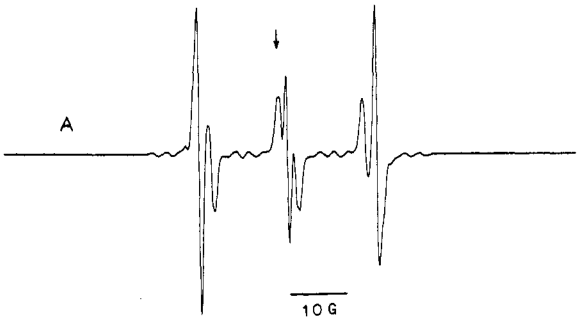

Figure 3. EPR spectrum of product from photolysis of **5**, DIPMA, and MNP.

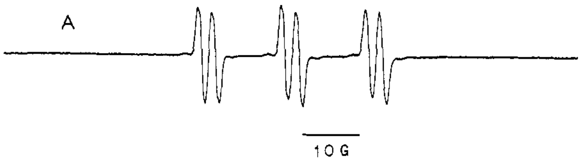

Figure 4. EPR spectrum of product from photolysis of **5**, DIPMA, and MNP after HPLC-EPR separation.

lyzed, and the solvent was evaporated. The EPR spectrum taken in benzene indicated a mixture of radicals, and two radical species were obtained by column chromatography. One had the triplet spectrum of di-*tert*-butyl nitroxide (a_N = 15.4 G), which can also be obtained by photolysis of MNP itself.[33]

$$(CH_3)_3CNO \xrightarrow{h\nu} NO^\bullet + {}^\bullet C(CH_3)_3$$
$$^\bullet C(CH_3)_3 + (CH_3)_3CNO \rightarrow [(CH_3)_3C]_2NO^\bullet \qquad (2)$$

The second radical isolated showed a triplets of doublets spectrum (Figure 2), which was identical with the previously obtained spectrum from the photolysis of TS with triethylamine.[17]

2. Para-Substituted *trans*-Stilbene with DIPMA. Using the procedure described above, the EPR spectrum (Figure 2) was not symmetrical, indicating a mixture of free radicals. Since the radicals were stable for at least 1 day, the mixture was subjected to HPLC separation with EPR as a detector. Two peaks were found in the chromatograph (Figure 1A,B). The spectrum of the fraction with retention time around 7.86 min (peaks b and d) was again the triplet spectrum of di-*tert*-butyl nitroxide (a_N = 15.4 G). The spectrum of the fraction with shorter retention time (7.19 min for peak a, 7.24 min for peak c) consisted of an unsymmetrical triplet of doublets, which indicates a mixture of radicals. Attempts to separate the mixture of radicals by using different columns as well as different solvent systems were unsuccessful. The EPR spectra for all the para-substituted TS were similar with all three tertiary amines.

3. Para,Para′-Disubstituted *trans*-Stilbene with DIPMA. Using the same procedure with para,para′-disubstituted *trans*-stilbenes **5–11**, a typical EPR spectrum (**5**) is shown in Figure 3. Separation by HPLC-EPR led to the two-peak chromatogram shown in Figure 1C,D. The EPR spectrum for peaks e and h (retention time 7.86 min) was that of di-*tert*-butyl nitroxide (a_N = 15.4 G). The fractions for peaks f and g could be separated easily from those of peaks e and h; the EPR spectrum from f is shown in Figure 4. These triplets of doublets spectra were identified by computational simulation. The hfsc for the nitrogens and the protons, as well as the *g* values, are listed in Table I.

Table I. Nitrogen and Proton Hyperfine Splitting Constants of Diphenylethyl Radical Spin Adducts of MNP in Benzene

X	σ_P	a_N	a_H	*g*
OCH_3	−0.20	14.58	2.39	2.0060
$(CH_3)_2CH$	−0.13	14.54	2.41	2.0059
CH_3	−0.14	14.53	2.42	2.0059
H	0.00	14.47	2.42	2.0060
Cl	0.22	14.43	2.40	2.0059
Br	0.22	14.42	2.39	2.0059
CN	0.71	14.25	2.38	2.0060

Discussion

The radicals isolated from HPLC-EPR studies are the di-*tert*-butyl nitroxide radical and the 1,2-diphenylethyl radical adduct **12**. By using a resolution-enhancement

$$PhCH_2\dot{C}HPh + MNP \rightarrow t\text{-}BuN(O^\bullet)C(Ph)HCH_2Ph \qquad (3)$$
$$\mathbf{12}$$

technique with Fourier transform deconvolution,[17] the hyperfine splitting constants of the radicals **12** were determined as a_N = 14.37 G, $a_H(\beta)$ = 2.17 G (1 H), $a_H(\gamma)$ = 0.56 G (2 H), $a_H(o,\beta\text{-Ph})$ = 0.15 G (2 H), $a_H(p,\beta\text{-Ph})$ = 0.26 G (1 H), $a_H(t\text{-Bu})$ = 0.09 G (9 H). The alternative chemical synthesis of the radical **12** was carried out by the Grignard reaction of benzylmagnesium bromide with α-phenyl-*tert*-butylnitrone (PBN)[1] (eq 4). The EPR spectrum of

$$PhCH_2MgBr + PBN \xrightarrow{H_2O}$$
$$PhCH_2CH(Ph)N(OH)Bu\text{-}t \xrightarrow{Ag_2O} PhCH_2CH(Ph)N(O^\bullet)Bu\text{-}t \qquad (4)$$

the radical so prepared was identical with that of the radical **12**. The long-range hfsc for radicals of eq 4 were $a_H(o,\beta\text{-Ph})$ + 0.13 G (2 H), $a_H(p,\beta\text{-Ph})$ + 0.288 G (1 H), and $a_H(t\text{-Bu})$ − 0.087 G (9 H) by analysis of the NMR spectrum of a concentrated solution of the radical.[17] These values are in good agreement with those obtained by analysis of the resolution-enhanced EPR spectrum of radical **12**. This radical has also been prepared by trapping the benzyl radical with the spin trap reagent PBN, but no long-range hfsc were reported.[8,34,35]

When para-substituted TS were irradiated with DIPMA, the products[36] isolated included regioisomers of the amine adduct **14**, **15** in a 1:1 ratio, regioisomers of the tetraphenylbutanes **16–18**, and the reduction product 1,2-diphenylethane (**19**). It is clear that the two 1,2-diphenylethyl radicals **20** and **21** are formed during photolysis by nonselective proton transfer from the aminium

$$\begin{aligned}
&trans\text{-}p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p + DIPMA \xrightarrow{CH_3CN} \\
&\quad cis\text{-}p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p\ (\mathbf{13}) + \\
&\quad C_6H_5CH_2CH(C_6H_4X\text{-}p)CH_2N(Pr\text{-}i)_2\ (\mathbf{14}) + \\
&\quad p\text{-}XC_6H_4CH_2CH(Ph)CH_2N(Pr\text{-}i)_2\ (\mathbf{15}) + \\
&\quad p\text{-}XC_6H_4CH_2CH(Ph)CH(Ph)CH_2C_6H_4X\text{-}p\ (\mathbf{16}) \\
&\quad + p\text{-}XC_6H_4CH_2CH(Ph)CH(C_6H_4X\text{-}p)CH_2C_6H_5\ (\mathbf{17}) + \\
&\quad PhCH_2CH(C_6H_4X\text{-}p)CH(C_6H_4X\text{-}p)CH_2Ph\ (\mathbf{18}) + \\
&\quad PhCH_2CH_2C_6H_4X\text{-}p\ (\mathbf{19}) \qquad (5)
\end{aligned}$$

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radical to the TS anion radical. When 20 and 21 were

$$\underset{\textbf{20}}{p\text{-}XC_6H_4\dot{C}HCH_2Ph} \qquad \underset{\textbf{21}}{Ph\dot{C}HCH_2C_6H_4X\text{-}p}$$

trapped by MNP, the retention times of the two trapped radicals were so similar that they could not be separated by HPLC. The EPR spectra of the para-substituted TS systems are all asymmetric, indicating a mixture of trapped radicals.

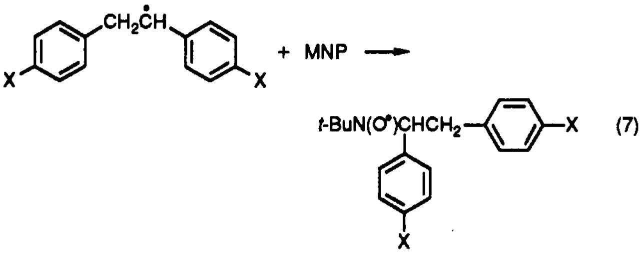
However, when para,para'-disubstituted TS were used instead of para-substituted TS, only one isomer of the amine adducts, the dimers, and the reduction products was found (eq 6). The radicals formed in the photolysis of

$$\begin{aligned} &trans\text{-}p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p + \text{DIPMA} \xrightarrow{CH_3CN} \\ &\quad cis\text{-}p\text{-}XC_6H_4CH{=}CHC_6H_4X\text{-}p\ (\textbf{22}) + \\ &\quad p\text{-}XC_6H_4CH_2CH(C_6H_4X\text{-}p)CH_2N(Pr\text{-}i)_2\ (\textbf{23}) + \\ &\quad p\text{-}XC_6H_4CH_2CH(C_6H_4X\text{-}p)CH(C_6H_4X\text{-}p)CH_2C_6H_4X\text{-}p \\ &\quad (\textbf{24}) + p\text{-}XC_6H_4CH_2CH_2C_6H_4X\text{-}p\ (\textbf{25}) \qquad (6) \end{aligned}$$

disubstituted TS include the di-*tert*-butyl nitroxide radical and the 1,2-(p,p'-X,X-phenyl)ethyl radical **26**. Trapping

$$\underset{\textbf{26}}{p\text{-}XC_6H_4CH_2\dot{C}HC_6H_4X\text{-}p}$$

by MNP afforded only one regioisomer of the nitroxide radical **27**. Since the EPR spectrum was symmetrical, the nitrogen and β-H hfsc could be obtained. The retention times for these trapped radicals were 7.3 and 8.2 min (Figure 1C,D).



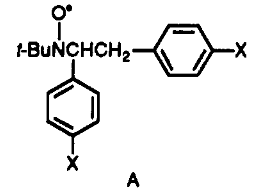
27

X = CH3O, *i*-Pr, CH3, H, Cl, Br, CN

The value of the nitrogen hfsc increases with increasing electron-withdrawing capability of the group at the para position of the phenyl group (Figure 5). This trend is similar to that observed for nitroxide radicals by Church[18] and Hanson.[37] The linear correlation is acceptable with a slope of −0.33 and correlation coefficient of 0.998. There is also a linear correlation in a dual parameter analysis. Using Taft's σ_R and σ_I, the linear correlation coefficient for the nitrogen hfsc is 0.998 (eq 8).

$$a_N = -0.432\sigma_R - 0.305\sigma_I + 14.48 \qquad (8)$$

The linear correlation of the nitrogen hfsc with the Hammett σ_P constants can be rationalized in terms of the two contributing resonance structures A and B for the nitroxide radical.



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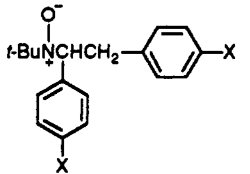

B

The dual parameter analysis indicates that the inductive and resonance effects are of equal importance.[18] The hyperfine coupling constants of the proton are relatively small (Table I), consistent with the G value of 1–5 for the methine proton.[38]

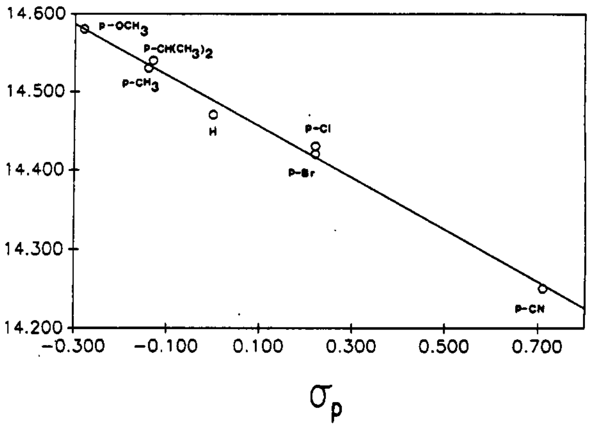

Figure 5. Plot of a_N of the trapped nitroxide radical **27** vs substituent constant σ_P.

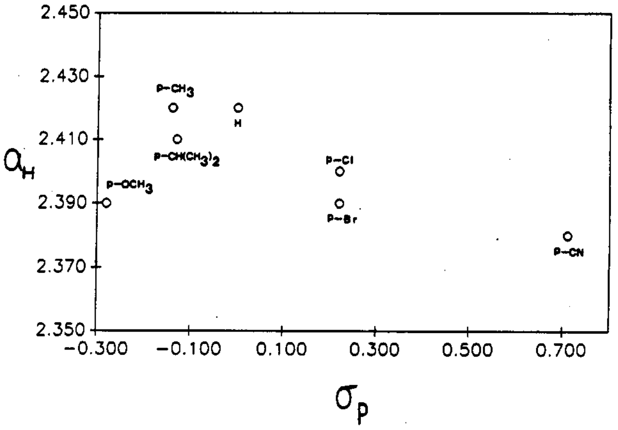

Figure 6. Plot of a_H of the trapped nitroxide radical **27** vs substituent constant σ_P.

The correlation of β-H hfsc with Hammett's σ_P is not linear (Figure 6). Church[18] has also reported the lack of correlation with β-H hfsc in trapping substituted phenyl radicals with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). This nonlinear correlation has been attributed to a through-space dipole–dipole interaction between the substituents and the benzylic C–H bond that alters the spin density at the hydrogen and affects the coupling between hydrogen and the radical. The magnitude of the β-H hfsc can be calculated from the Heller–McConnell equation.[39]

$$A^{\beta}{}_H = B_1 + B_2 \cos^2 \Theta \qquad (9)$$

B_1 and B_2 are constants, $B_1 \approx 0$ and $B_2 \approx 26$ G for nitroxides, and Θ is the dihedral angle between the nitrogen π orbital and the N–C–H plane. The observed values of β-H hfsc ranged from 2.39 to 2.44 G, corresponding to a dihedral angle of ~72° (eq 9), whereas the value of ~19 G for the β-H hfsc observed by Church corresponds to a dihedral angle of only ~30°. Even though the β-H hfsc shows no correlation with σ_P or $\sigma^+{}_P$, $\sigma^-{}_P$, there is moderate correlation (correlation coefficient 0.92) when the dual parameters σ_R and σ_I are used (eq 10). Here, the inductive

$$a_H = 0.0046\sigma_R - 0.0538\sigma_I + 2.42 \qquad (10)$$

effect plays a more important role in the linear correlation. The moderate correlation with dual parameters reflects

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the fact that the substituted phenyl group in our nitroxide radical is much closer to the N π orbital, increasing the inductive interaction. This result agrees with the report of Janzen[40] that the phenyl ring tends to line up with the nitroxyl p-π orbital.

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Registry No. 1, 1694-19-5; 2, 1657-50-7; 3, 13041-70-8; 5, 15638-14-9; 6, 37163-82-9; 7, 18869-29-9; 8, 103-30-0; 9, 1657-56-3; 10, 18869-30-2; 11, 134735-76-5; 27 (X = OMe), 134735-77-6; 27 (X = *i*-Pr), 134735-78-7; 27 (X = Me), 134735-79-8; 27 (X = H), 21894-25-7; 27 (X = Cl), 134735-80-1; 27 (X = Br), 134735-81-2; 27 (X = CN), 134735-82-3; TEA, 121-44-8; DIPEA, 7087-68-5; DIPMA, 10342-97-9; PBN, 3376-24-7; benzylmagnesium bromide, 1589-82-8.

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Reactivity of the Thiazolium C2 Ylide in Aprotic Solvents: Novel Experimental Evidence for Addition Rather Than Insertion Reactivity

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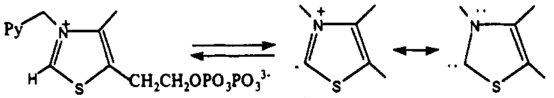
Two thiazolium compounds were synthesized specifically labeled at their C2 positions: 3,4,5-trimethyl[2-^{13}C]thiazolium nitrate and 3-benzyl-5-(β-ethoxyethyl)-4-methyl[2-^{13}C]thiazolium bromide, with a view to examine their pathways leading to dimerization in strongly basic medium using ^{13}C NMR. On addition of less than 1 equiv of base the *N*-methyl ion first formed an unsymmetrical dimer in which the C2 atoms of two molecules were bonded to each other and only one of them still carried a hydrogen; that unsymmetrical dimer upon addition of excess base lost the remaining hydrogen at C2 and was converted to a mixture of syn and anti symmetrical dimers in nearly equal amounts. The sequence of observations on addition of base to the *N*-methyl derivative is consistent with nucleophilic addition of the conjugate base to a second thiazolium ion at its C2 position. Since the unsymmetrical dimer is formed first, rather than the symmetrical dimer, the latter cannot result from direct dimerization of two conjugate bases (ylides) by a carbene mechanism. Instead, a carbanion-addition mechanism was further supported by two experiments. A "crossover" experiment was designed in which unsymmetrical dimers were detected in Me_2SO on addition of limiting potassium *tert*-butoxide to thiazolium ions containing [2-^{13}C]-H and [2-^{12}C]-D, under conditions such that there was little H/D exchange observed at the C2 position. Also, *N*-3-alkenylthiazolium ions were synthesized, that, if carbenic reactivity had existed, would have resulted in formation of cyclopropanes. In preference to the intramolecular reaction, intermolecular unsymmetrical dimers resulted in each case, consistent with nucleophilic addition. On addition of base to the *N*-benzylthiazolium ion, the first product to be detected by ^{13}C NMR was the syn/anti symmetrical dimer mixture (again bonded via the C2 atoms), that underwent a [1,3]-sigmatropic rearrangement of one of the benzyl groups from N3 to C2. According to ^{1}H NMR recorded within minutes of mixing, the unsymmetrical dimer precedes the symmetrical one for this salt as well. The reactivity of the C2 ylide derived from the *N*-methyl and *N*-benzylthiazolium ions can be rationalized according to an ionic addition reaction, implying that the related thiamin (vitamin B_1) conjugate base (ylide) behaves similarly.

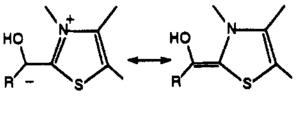
Introduction

The chemistry of thiamin diphosphate (**1a**) dependent enzymes is governed by the very unusual properties of two highly conjugated chemical structures: the ylide **1b**, obtained by deprotonation of the thiazolium ring at C2, and the C2α carbanion (or enamine, **2**) obtained upon decarboxylation of the most prevalent substrate for such enzymes, i.e. α-keto acids.[1] In recent years, we reported quantitative generation of enamines **2** from the corresponding 2-alkyl- and 2-benzylthiazolium salts in aprotic solvents by the addition of nonnucleophilic bases so as to avoid nucleophilic addition, and subsequent ring opening at C2.[2] The pK_a's at the C2α position were recently determined in Me_2SO for a number of 2-alkyl- and 2-benzylthiazolium salts,[3] indicating that in Me_2SO that position possesses stronger thermodynamic acidity than hitherto assumed. In addition, the facile electrochemical one-electron oxidation of the enamines was also reported.[4] In recent reports the pK_a for ylide generation in water was revised upward from its previous value of 12.7 determined



1a Ylide **1b** Carbene (1)

Py= 5- (4-amino-2-methyl)pyrimidinyl



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